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Immobilization of elemental mercury by biogenic Se nanoparticles in soils of varying salinity

Xiaonan Wang [a,c,d], Xiangliang Pan [a,b,*], Geoffrey Michael Gadd [d]

[a] *Xinjiang Key Laboratory of Environmental Pollution and Bioremediation, Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, Urumqi 830011, China*

[b] *College of Environment, Zhejiang University of Technology, Hangzhou 310014, China*

[c] *University of Chinese Academy of Sciences, Beijing 100049, China*

[d] *Geomicrobiology Group, School of Life Sciences, University of Dundee, Dundee DD1 5EH, Scotland, UK*

*For correspondence. E-mail panxl@zjut.edu.cn; Tel. +86 571 88320634; Fax +86 571 88320634.

ABSTRACT

Salinity can be a significant environmental stress which can govern the fate of nanoparticles in the environment as well as other factors such as pH, natural organic matter and minerals. In this research, the effects of salinity on the behaviour of biogenic selenium nanoparticles (BioSeNPs) and consequences for elemental mercury (Hg^0) immobilization in soil and soil solutions were investigated. It was found that homoaggregation and sedimentation of BioSeNPs were enhanced significantly with increasing salinity. Compression of the electric double layers of BioSeNPs at high ionic strengths resulted in attractive van der Waals forces dominating and leading to enhanced aggregation. Moreover, neutralization of the surface negative charge of BioSeNPs by divalent cations and the bridging of BioSeNPs via calcium binding to surface functional groups were also associated with enhanced aggregation. Such enhanced aggregation exerted inhibition of Hg^0 immobilization in soil solutions/soils of varying salinity. These results indicate that salinity is an important environmental factor governing aggregation of BioSeNPs and therefore influencing the efficiency of Hg^0 immobilization, and possible remediation treatments, as a consequence.

Keywords: selenium nanoparticles; salinity; aggregation; mercury immobilization

1. Introduction

Nanoparticles (NPs) are materials having any external dimension in the nanoscale or with an internal/surface structure in the nanoscale (Magdolenova et al., 2014). NPs are receiving huge attention due to their unique properties such as size, surface structure, shape and high reactivity (Shelley, 2005; Farré et al., 2009). Around 40–50% of the atoms in NPs are on the surface, meaning that NPs can have special biological effects unlike their micro- and macro scale counterparts (Auffan et al., 2009). NPs have been widely used in textiles, cosmetics, electronic devices, disease diagnostics and remediation of contaminated environments (Schmid, 2010; Ju-Nam and Lead, 2008). It is known that biogenic selenium nanoparticles (BioSeNPs) have a stronger mercury (Hg) capture capacity (188 mg Hg g^{-1}) than chemically synthesised SeNPs or SeNPs at the micro/macro scale (Johnson et al., 2008). Moreover, BioSeNPs have been demonstrated to be an effective bioremediation technique for immobilization of elemental mercury (Hg^0) in soil and water because of the reaction: $Hg^0 + Se^0 \rightarrow HgSe$ ($\Delta G^0 = -38.1$kj mol^{-1}) (Wang et al., 2017; 2018a).

With the increasing development of nanotechnology, large amounts of NPs have been released into the environment and their fate is considered to be an emerging environmental concern. NPs in the environment are subject to a wide range of processes: homoaggregation, adsorption of dissolved organic matter,

complexation by ions, heteroaggregation to particulate matter and subsequent sedimentation, dissolution and chemical transformation. Environmental factors such as salinity, ionic strength, pH, organic matter and clay minerals are the most significant parameters governing the fate of NPs in the environment (Baalousha et al., 2013; Zhu et al., 2014; Wang et al., 2019).

Salinity is a major environmental stress, and the term refers to the presence of major dissolved inorganic solutes especially Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cl^{-}, SO_4^{2-}, HCO_3^{-} and CO_3^{2-} in solution, and is associated with soluble and readily dissolvable salts in soil (Rhoades, 1996). Salinity can have a significant influence on metal ion speciation. For example, increasing salinity can decrease concentrations of Cu^{2+} and Zn^{2+} due to precipitation and complexation, and alleviate toxicity (Park et al., 2014). Research on the role of salinity in determining the bioavailability and toxicity of NPs has received current interest (Kataoka et al., 2015; Qin et al., 2017). For instance, a reduced electrical double layer (EDL) resulted in an increased hydrodynamic diameter of AgNPs with increasing salinity, and AgNPs were likely to agglomerate to a larger size under high salinity than for low salinity (Joo et al., 2013). In general, greater salinity can lead to lower toxicity of NPs since lower concentrations of metal ions may be released from metal and metal oxide NPs (Yung et al., 2017). However, in contrast, the toxicity of polyvinylpyrrolidone-coated AgNPs increased

significantly with increasing salinity although the toxicity of Ag^{+} decreased (Macken et al., 2012). To date, most of the work on the effects of salinity on NPs are carried out in natural seawater, artificial seawater and saline solutions prepared with chemicals such as NaCl and $CaCl_2$ (Kim et al., 2015; Yung et al., 2015). Less attention has been paid to soil salinity which has a different composition to seawater. It is known that 6% of the total land area of the world is affected by salt (Munns and Tester, 2008). It is therefore of great importance to understand the impact of salinity on the stability, transport and environmental fate of NPs because of the increasing environmental applications of nanotechnology.

In this work, the effects of salinity on BioSeNPs and consequences for Hg^0 immobilization were investigated. A soil solution and soil with varying salinity were prepared using natural salt extracted from a saline soil. Homoaggregation of BioSeNPs in a variety of saline solutions was examined using time-resolved dynamic light scattering, sedimentation of BioSeNPs was examined in settling experiments, and the effects of salinity on Hg^0 immobilization using BioSeNPs in soil and soil solution of differing salinity were assessed by the measurement of residual concentrations of Hg^0 using a mercury analyzer and determination of mercury speciation.

2. Materials and methods

2.1 Preparation of saline solution/soil and BioSeNPs

Natural salt was extracted from a saline soil as follows. 1 kg saline soil was collected from the Korla area, Xinjiang, China and mixed with 5 L Milli-Q water using overhead stirrers for 18 h. This process was repeated several times to make sure that the salt in the saline soil was dissolved completely. Afterwards, the soil particles were allowed to settle in Milli-Q water and the supernatant was filtered through filter-paper to obtain a solution containing natural salt. This solution was then heated in an electric furnace to obtain salt through evaporative crystallization. 30% hydrogen peroxide was added to remove organic matter, and the collected salt was finally oven dried. The settled washed desalinated soil was air dried for future use. Reconstituted soil solution/soil of varying salinity (0, 0.2, 1, 3, 5, 10%) was prepared artificially by dissolving appropriate amounts of natural salt in Milli-Q water/air dried settled desalinated soil. Electric conductivity, pH, and concentrations of K^+, Ca^{2+}, Na^+, Mg^{2+}, Cl^- and SO_4^{2-} were determined as described previously (Wang et al., 2018a).

Biogenic SeNPs (BioSeNPs) were obtained through the reduction of sodium selenite (1 mM) by *Citrobacter freundii* Y9, with the collected BioSeNPs from culture supernatants being purified according to Cui et al. (2016) and freeze-dried for future use. Purified BioSeNPs were characterized using transmission

electron microscopy with energy-dispersive X-ray spectrometry (TEM-EDS) (FEI Tecnai G2 F20 S-TWIN, Houston, USA) and X-ray diffraction (XRD) (Bruker D8, Karlsruhe, Germany). A single drop of BioSeNPs solution was dried on a 200-mesh copper TEM grid for TEM-EDS examination. The X-ray diffractometer was equipped with a Cu anode (40 kV and 30 mA) and scanning was from 5 to 80^{o} 2θ, and phase identification was carried out as previously described (Luo et al., 2018).

2.2 Zeta potential

The zeta potential of BioSeNPs (50 mg L^{-1}) as a function of pH over the range pH 3-10 in varied saline solutions (0, 0.2, 1, 3, 5, 10% (w/v)) was measured using a Zetasizer Nano ZS90 (Malvern, Worcestershire, UK).

2.3 Aggregation

The homoaggregation of BioSeNPs (50 mg L^{-1}) in saline solution (0, 0.2, 1, 3, 5, 10%) was determined by time-resolved dynamic light scattering (DLS) (Malvern Zetasizer Nano ZS90, Worcestershire, UK). Based on the profiles of homoaggregation, the initial aggregation constant (k) was calculated from the increase of $D_h(t)$ with time (t) as shown in equation 1, and the attachment

efficiency (α) obtained by normalizing k to k_{fast} as presented in equation 2 (Schudel et al., 1997; Huynh and Chen, 2011; Huangfu et al., 2013).

$$k \propto \frac{1}{N_0}\left\{\frac{dD_h(t)}{dt}\right\}_{t\to 0} \quad (1)$$

N_0: original concentration of BioSeNPs

$D_h(t)$: the hydrodynamic diameter of BioSeNPs at different times

$$\alpha = \frac{k}{k_{fast}} = \frac{\frac{1}{N_0}\left\{\frac{dD_h(t)}{dt}\right\}_{t\to 0}}{\frac{1}{(N_0)_{fast}}\left\{\frac{dD_h(t)}{dt}\right\}_{t\to 0,fast}} \quad (2)$$

k_{fast}: diffusion-limited aggregation rate constant of particles determined under favourable conditions

2.4 Settling experiments

Settling experiments for 50 mg L^{-1} BioSeNPs were conducted in saline solutions (0, 0.2, 1, 3, 5, 10% (w/v)) according to protocols reported previously (Wang et al., 2018a).

2.5 Hg immobilization using BioSeNPs in saline solution/soil

The immobilization of Hg^0 using BioSeNPs was carried out in Hg^0-contaminated saline solution and saline soil separately. The extracted natural salt was added to Hg^0-contaminated Milli-Q water as described by Gai et al. (2016). to provide a Hg^0-contaminated solution of varying salinity (0, 0.2, 1, 3, 5, 10% (w/v)). BioSeNPs were added to a final concentration of 50 mg L^{-1} to the Hg^0-contaminated saline solution and shaken for 6 h after which time the residual Hg^0 remaining in solution was measured using a Hg analyzer (Lumex RA915+, Saint Petersburg, Russia). The preparation of Hg^0-contaminated solution, instrument setup and settings for Hg analysis are described in detail in our previous work (Wang et al., 2018b). Differences in the residual Hg^0 content remaining in the solution among salinity were tested using one-way ANOVA, and differences and correlations were considered statistically significant if $p < 0.05$. The statistical test was performed using SPASS 22.0 (SPSS Inc., USA). The precipitate formed after treated with BioSeNPs in saline solution was collected and analysed using TEM-EDS and XRD.

Liquid mercury was added directly to the air-dried settled desalinated soil, and after that, the appropriate amount of natural salt was added to the soil and fully mixed to prepare saline soil of varying salinity (0, 0.2, 1, 3, 5, 10%) and aged for one month. Mercury immobilization experiments were performed in

centrifuge tubes which contained 10 g Hg^0-contaminated soil of given salinity. 10 ml Milli-Q water containing 50 mg L^{-1} BioSeNPs was added to the tubes which were shaken for one week to immobilize the Hg^0. A modified sequential extraction procedure, as described in Wang et al. (2017), was used to measure mercury speciation including total mercury, elemental mercury, bioavailable mercury, mercury bound to organic matter and residual mercury in the different saline soils before and after Hg^0 immobilization, according to previous research (Biester and Scholz, 1996; Shi et al., 2005).

3. Results

3.1 Saline solution/soil and BioSeNPs

The physico-chemical properties of the saline solution and soil are shown in Tables S1 and S2, respectively. The BioSeNPs synthesized by *Citrobacter freundii* Y9 were amorphous SeNPs (Fig. S1).

3.2 Zeta potential

BioSeNPs carried a negative charge over the pH range 3-11 in the different saline solutions as shown in Fig. 1. BioSeNPs were negatively charged, and this increased with increasing pH in Milli-Q water. It was found that the negative charge of BioSeNPs in a saline solution was lower than that in Milli-Q water. Over the range pH 6-8, the magnitude of negative charge followed the order: BioSeNPs in Milli-Q water (~ -20.2 mV) > BioSeNPs in solution (0.2% salinity) (~ -11.6 mV) > BioSeNPs in solution (1% salinity) (~ -7.1 mV) > BioSeNPs in solution (3% salinity) (~ -5.4 mV) > BioSeNPs in solution (5% salinity) (~ -4.2 mV) > BioSeNPs in solution (10% salinity) (~ -3.0 mV).

{ EMBED Origin50.Graph }

Fig. 1. Zeta potential of BioSeNPs as a function of pH in differing saline solution. Symbols represent: (■) zero salinity; (□) 0.2% salinity; (●) 1% salinity; (○)

3% salinity; (▲) 5% salinity; (△) 10% salinity. Error bars represent the standard deviation (n=3).

3.3 Aggregation

Homoaggregation profiles of BioSeNPs in various saline solutions are shown in Fig. 2. The hydrodynamic diameter of BioSeNPs increased over a time period of 1 h, and seemed to increase significantly with greater salinity. The attachment efficiencies (α) of BioSeNPs in saline solution, which were calculated based on homoaggregation profiles, significantly increased with increasing salinity (Fig. 3).

{ EMBED Origin50.Graph }

Fig. 2. Homoaggregation profiles of BioSeNPs in solutions of varying salinity. Symbols represent: (■) zero salinity; (●) 0.2% salinity; (▲) 1% salinity; (▼) 3% salinity; (◆) 5% salinity; (★) 10% salinity. Typical results are shown from one of several determinations.

{ EMBED Origin50.Graph }

Fig. 3. Attachment efficiencies of BioSeNPs in various saline solutions. Error bars represent the standard deviation (n = 3)

3.4 Settling experiments

The settling of BioSeNPs reached equilibrium over a 16 h time period, and the settling efficiency of the BioSeNPs increased with increasing salinity which was in the order: SeNPs in 10% salinity (~ 44.8%) > SeNPs in 5% salinity (~ 42.0%) > SeNPs in 1% salinity (~ 31.3%) > SeNPs in 3% salinity (~ 30.2%) > SeNPs in 0.2% salinity (~ 25.1%) > SeNPs in Milli-Q water (~ 21.2%) (Fig. 4).

{ EMBED Origin50.Graph }

Fig. 4. Settling of BioSeNPs in different saline solutions. C_i is the concentration of BioSeNPs detected at specific times; C_0 is the initial concentration of BioSeNPs. The concentration of BioSeNPs was assessed using the OD_{260nm} of the suspension. Symbols represent: (■) zero salinity; (□) 0.2% salinity; (●) 1% salinity; (○) 3% salinity; (▲) 5% salinity; (△) 10% salinity. Error bars represent the standard deviation (n = 3).

3.5 Hg immobilization using BioSeNPs in saline solution/soil

The effect of salinity on Hg^0 immobilization using BioSeNPs in a soil solution are shown in Fig. 5. The residual content of Hg^0 was 891.9 ng in the control, and the Hg^0 content was significantly reduced to 18.2 ng with a 98.0% removal efficiency in the presence of 50 mg L^{-1} BioSeNPs. The residual Hg^0 content in soil solution was significantly changed ($p < 0.05$) and it was found that Hg^0 removal efficiency decreased from 98.0% to 92.7-97.5% under saline conditions. Hg^0 removal was most significantly affected at 0.2% salinity with the

removal performance decreasing from 98.0% to 92.7%. In the soil solution with salinities ranging from 1-10%, the Hg^0 removal efficiency only slightly declined from 98.0% to 96.4-97.5%. The precipitate that formed in the BioSeNPs treated saline solution was composed mainly of Hg and Se, and the mapping scans of Hg and Se were highly in accordance with their distribution in the precipitate (Fig. S2). XRD analysis further revealed that the precipitate was HgSe (Fig. S3).

{ EMBED Origin50.Graph }

Fig. 5. Residual Hg^0 content in various saline solutions after Hg^0 immobilization using 50 mg L^{-1} BioSeNPs. The control was conducted without addition of SeNPs. Symbols represent: ■ control; □ zero salinity; ▨ 0.2% salinity; ▤ 1% salinity; ▧ 3% salinity; ▦ 5% salinity; ▥ 10% salinity. Error bars represent the standard deviation (n=3). Values followed by the same letter do not differ significantly at the 5% level according to one-way ANOVA.

The Hg^0 immobilization efficiency of BioSeNPs in Hg^0-contaminated soil under saline conditions is shown in Fig. 6. For the control, the total Hg content was 3049.3 ng, and most of the Hg occurred as Hg^0 (2909.3 ng) which accounted for 95.4%. Residual Hg was another important fraction (122.5 ng) accounting for 4.0% of the total Hg. Bioavailable Hg and organic mercury were negligible fractions of the total Hg, and only comprised 0.6% of the total Hg. After addition of 50 mg L^{-1} BioSeNPs at zero salinity, the Hg^0 fraction decreased markedly to

12.7%. However, the residual Hg fraction increased to 87.3%. It is interesting that the percentage of Hg^0 of the total Hg increased from 13.2% to 31.9% and the percentage of residual Hg decreased from 86.7% to 68.0% when the salinity of soil was increased from 0.2% to 10%.

{ EMBED Origin50.Graph }

Fig. 6. The percentage of different fractions of Hg in the various saline soils after treatment with 50 mg L^{-1} BioSeNPs. The control was conducted without the addition of BioSeNPs. Symbols represent: ☐ residual Hg; ■ bioavailable Hg; ■ organic Hg; ■ elemental Hg. Error bars represent the standard deviation (n=3).

4. Discussion

It has been reported that homoaggregation of nanoparticles in aquatic solution is affected by the chemical properties of the solution such as salinity, ionic strength, pH, and cation valency (French et al., 2009; Loosli et al., 2015; Ellis et al., 2016; Yang et al., 2019). Some research has shown that salinity rather than dissolved organic matter is the dominating factor that governs the stability, and especially the aggregation, of TiO_2 and Ag NPs (Wang et al., 2014). Therefore, it is desirable to understand the role of salinity on the aggregation of BioSeNPs and any consequences for Hg immobilization.

A large amount of research has found that salinity has a great impact on the bioavailability and toxicity of nanoparticles in the environment, and this is highly related to the aggregation properties of the nanoparticles (Kataoka et al., 2015; Qin et al., 2017). For example, the effect of AgNPs on certain aquatic biota was associated with the release of Ag^+ or the uptake of nanoscale particles: suspended nanoparticles are likely to cause more negative effects than agglomerated nanoparticles. It was demonstrated that the presence of electrolytes and high ionic strength in a highly saline solution can lead to an increase in AgNPs hydrodynamic diameter which resulted in AgNPs agglomerating to a larger size. Moreover, the decreased surface area of the aggregated AgNPs also decreased the capacity for releasing Ag^+ from AgNPs surfaces (Griffitt et al.,

2008; Joo et al., 2013). This is similar to our results where homoaggregation of BioSeNPs was enhanced with increasing salinity. One explanation is that the outer shell of the electric double layers (EDLs) of nanoparticles are compressed with increasing salinity, which provides a higher ionic strength, meaning that attractive van der Waals forces dominate and lead to enhanced aggregation (Bian et al., 2011). Several works have found that a colloid concentration decreases dramatically because of aggregation and precipitation with increasing salinity (Stolpe and Hassellöv, 2007). Yung et al. (2017) demonstrated that ZnO nanoparticles formed larger aggregates and released less Zn^{2+} in high salinity. Park et al. (2014) demonstrated that aggregation and dissolution of CuO and ZnO nanoparticles was affected by salinity and this played an important role in controlling NPs toxicity to *Tigriopus japonicus*.

The enhanced homoaggregation of BioSeNPs in solutions of high salinity is also related to the presence of divalent cations, e g Ca^{2+} and Mg^{2+}. Zhang et al. (2009) reported that the surface charge of nanoparticles could be neutralized by divalent cations such as Ca^{2+} leading to eventual aggregation. Complexation between Ca^{2+} and carboxyl groups on the surface of citrate-AgNPs decreased the zeta potential and also enhanced aggregation (Badawy et al., 2010). Our data is in agreement with these findings. Ca^{2+} and Mg^{2+} increased from 6.57 and 179.22 mg L^{-1} to 807.23 and 8432.90 mg L^{-1}, respectively, when the salinity increased

from 0.2 to 10%. However, the zeta potential of BioSeNPs decreased from -20.3 to -3.2 mV over the pH range 6-8 when the salinity increased from 0 to 10%. Neutralization by divalent cations decreased electrostatic repulsion resulting in enhanced aggregation. There is a clear relationship between zeta potential and attachment efficiency. Electrostatic repulsion is high and α is nearly zero at very negative zeta potential values, and electrostatic repulsion is almost zero and α is nearly unity when the zeta potential is nearly zero. Moreover, Ca^{2+} can enhance aggregation by forming calcium-bridges between nanoparticles (Chen and Elimelech, 2007). Calcium readily binds to surface functional groups, such as those present in EPS, and this strong affinity can result in interlinking of polymer chains on the surfaces of BioSeNPs (Chen et al., 2007; Jain et al., 2015). Ranka et al. (2015) also demonstrated that Ca^{2+} had an important impact on a polymer coating on nanoparticles, and a stabilizing polyelectrolyte coating would typically fail at high salinities because of dehydration and excessive charge screening.

However, some contrasting research has shown that some kinds of nanoparticles do not readily aggregate under saline conditions. For example, increasing salinity decreased the toxicity of Ag^{+}, although the toxicity of polyvinylpyrrolidone-coated AgNPs increased. This increase in toxicity was most likely to be associated with a combination of the surface properties of nanoparticles and their reactivity within highly saline media (Kim et al., 2015).

The effects of salinity on nanoparticles are therefore not only related to the properties of the solution but also associated with the properties of the nanoparticles. The coatings and functional groups on the surfaces of nanoparticles govern how nanoparticles interact with each other and other components in solution which also play a part in controlling the effects of salinity (Navarro et al., 2008; Scown et al., 2010). Booth et al. (2013) found that polymeric nanoparticles (PNPs) synthesised with a non-ionic stabilising agent (Lutensol AT50) could remain in suspension even at 100% salinity compared with PNPs formed with the ionic stabiliser sodium dodecyl sulphate (SDS). One reason for this is that the absence of ionic groups on the surface of nanoparticles means they cannot be impacted by the saline environment. On the other hand, the effects of salinity on nanoparticles are also related to the hydrophobicity/hydrophilicity of the material, since synthesised and purified PNPs with higher hydrophobicities are likely to aggregate under higher saline conditions.

Nanoparticles undergoing aggregation will settle by gravity especially if the size of the aggregates is greater than 1 μm. According to previous work, sedimentation rates were very high for ZnO, CeO_2 and TiO_2 nanoparticles in seawater of high salinity (Keller et al., 2010). This is in accordance with the results presented here where enhanced aggregation due to a compressed electric

double layer, charge neutralization and calcium-bridging led to a greater settling efficiency.

It is known that the unique properties and high reactivity of nanoparticles results from their huge surface area to volume ratio. Enhanced aggregation and settling significantly reduce the surface area and therefore block the access of nanoparticles to other materials. Amorphous BioSeNPs can be used for Hg immobilization from air and water, and in soil because of their strong Hg^0 capturing capacity (Wang et al., 2017; 2018a, b). Environmental factors such as extracellular polymeric substances and goethite can affect Hg^0 immobilization efficiency (Wang et al., 2018a, b). In the present work, increasing salinity in the solution inhibited Hg^0 immobilization using BioSeNPs, but the inhibitory effect was not significantly enhanced with increasing salinity. One reason may be that the electric double layer could not be compressed further with increasing salinity, so the effects of salinity on Hg^0 immobilization in saline solution were not so obvious (Yung et al., 2015). Nevertheless, Hg^0 immobilization efficiency was significantly suppressed in saline soil, and the proportion of Hg^0 transformed to residual Hg by BioSeNPs significantly decreased with increasing salinity, which may be associated with the heterogeneity and complexity of soil. Another important factor may be associated with reduced Hg^0 immobilization with increasing soil salinity. A range of interactions can occur between dissolved

organic matter (DOM) and nanoparticles in soil, the most important being adsorption (Philippe and Schaumann, 2014). DOM can adsorb to the surface of nanoparticles in spite of any initial coating (Stankus et al., 2011). Divalent and trivalent cations were also demonstrated to enhance adsorption of DOM onto nanoparticles (Schlautman and Morgan, 1994; Janot et al., 2010). Erayhem et al. (2014) found that Mg^{2+} and Ca^{2+} promoted adsorption of DOM onto TiO_2 nanoparticles through surface charge screening and cation bridging. Increased ionic strength can also enhance the adsorption of DOM on mineral colloids (Zhou et al., 1994; Feng et al., 2005).Thus, increased ionic strength and concentrations of divalent cations caused by increasing salinity may contribute to the adsorption of DOM on BioSeNPs in soil. Such adsorption of DOM onto BioSeNPs could inhibit Hg^0 access to the surface of BioSeNPs and thus lead to inhibition of Hg^0 immobilization.

5. Conclusions

Salinity can play a significant role in governing the environmental fate of BioSeNPs. Compressed electric double layers and dominating van der Waals forces under high ionic strength, charge neutralization due to complexation by divalent cations and calcium-bridges all contribute to enhanced aggregation and sedimentation under saline conditions. On aggregation, Hg^0 immobilization was suppressed because of the decreased surface area and reduced access sites of the

BioSeNPs, and the inhibitory effect was more obvious with increasing salinity in soil rather than in soil solutions.

Conflict of interest

The authors declare no competing financial interest.

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